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Hydration and Setting Behaviour of Strontium Aluminate Cements

Hydration of cement generally means complex changes and reactions which occur when the cement paste is prepared by mixing of anhydrous cement with water. Setting means stiffening without significant development of compressive strength which typically occurs within a few hours after mixing of cement with water. Hardening process means gradual significant development of compressive strength during curing in applied environmental conditions (storage in air or water, temperature) [263,265,270].

As was already mentioned in Chapter 2.6, cement slurries are complex reactive systems. They continuously change, physically and chemically. The microstructural and chemical evolution of cement slurry from the first minutes after mixing of cement powder with water until the beginning of setting can be observed by a variety of physicochemical methods including thermal analysis calorimetry [286-393], X-ray diffraction analysis [386,394,744], infrared Raman and Mössbauer spectroscopy [386,395,396], electron microscopy [273,275,394-399] as well as via liquid phase analysis [400,401], porosity and specific surface of cement stone measurement [402], ultrasonic pulse velocity [403-406], impedance spectroscopy measurement [407,408] and electrical conductivity/ resistivity measurement [409,410].

The knowledge of the setting characteristics of concrete is quite important in the field of concrete construction. They will help in scheduling of various stages involved in concrete construction operations such as transporting, placing, compacting and finishing of concrete. This information is a necessity when deciding whether to use a retarding admixture or accelerator or not [411].

The introduction of superplasticizers in early 1960s had great effect on the development in concrete technology. Superplasticized cement can be prepared with lower water to cement ratio, has improved workability, high strength and high durability without affecting the setting and hardening behaviour. In chemical terms, superplasticizers are organic polyelectrolytes which belong to the category of polymeric dispersants. Today, superplasticizers are considered as an integral component of High-Performance concretes [412].

ASTM C494 recognizes the following classes of superplasticizers [412]:

1. **Class F:** High-range water reducers: the most important group are sulphonated synthetic polymers such as poly- β -naphtalene sulphonate and sodium polymelamine sulphonate;
2. **Class G:** High-range water reducers and retarders.

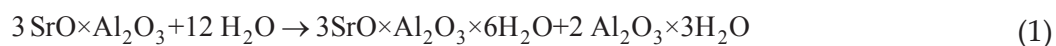
Further sub-classifications of superplasticizers is also used and refers to the first, second and third generation of products.

The effect of superplasticizers' chemical structure on their efficiency in cement pastes was investigated by Janoska-Rekans [413]. The efficiency of industrial superplasticizers increases with the molecular weight of the superplasticizer polymer as well as with its mass fraction in considered sample. The efficiency of a superplasticizer increases with its hydrophilicity. The hydrophilic nature of the superplasticizer polymers can be measured as the ratio of ethers to esters.

General effect of admixtures such as silica fume, metakaolinite, fly ash and blast-furnace slag is the retardation of setting time of high-strength concrete [411]. Regarding limestone, the higher the limestone fines content in the mix, the shorter the initial and final setting times of concrete [414,415].

1. Analysis of hydration products

The compounds formed during 28 days of hydration of strontium aluminate clinker were investigated by X-ray diffraction analysis (Fig.1). The cubic tri-strontium aluminate hexahydrate phase (Sr_3AH_6) and the high alumina gel phase (AH_3 gel) are recognized as the main products of hydration:



That enables to calculate the theoretic water to cement ratio for the hydration of strontium aluminate cement to be 0.36. SrAH_{7-10} hydrate and gibbsite ($\gamma\text{-AH}_3$) appear after 7 and 14 days of hydration, respectively. The rate of the hydration process is significantly reduced after 14 days and the sample still contains about 20 % of unhydrated strontium aluminate phase in the 28th day of hydration (Fig.2).

The phase composition of strontium aluminate cement during the first 24 hours of hydration process is shown in Fig.3. These data confirm that tri-strontium aluminate hexahydrate is the only crystalline hydration product during early stages of hydration of strontium aluminate clinker and the initial rate of hydration is very fast as the results from calorimetric measurements show (Chapter 5.2). From this reason some important compounds improving the reactivity of strontium aluminate cement must be used in order to reach better workability (Chapter 5.4).

The infrared spectra (Fig.3) show sharp absorption band at 3664 cm^{-1} , which is related to the stretching of OH groups of Sr_3AH_6 . The dehydration of this phase shows sharp endothermic peak at the temperature of 262°C on TG-DTA and EGA (Fig.5). The test piece area decreases in about 6.0 % during this process (Fig.28 in Chapter 4). The dehydration of the gel phase shows an endothermic effect on DTA at the temperature of 198°C , but the peak intensity and the temperature decrease with the time of hydration.

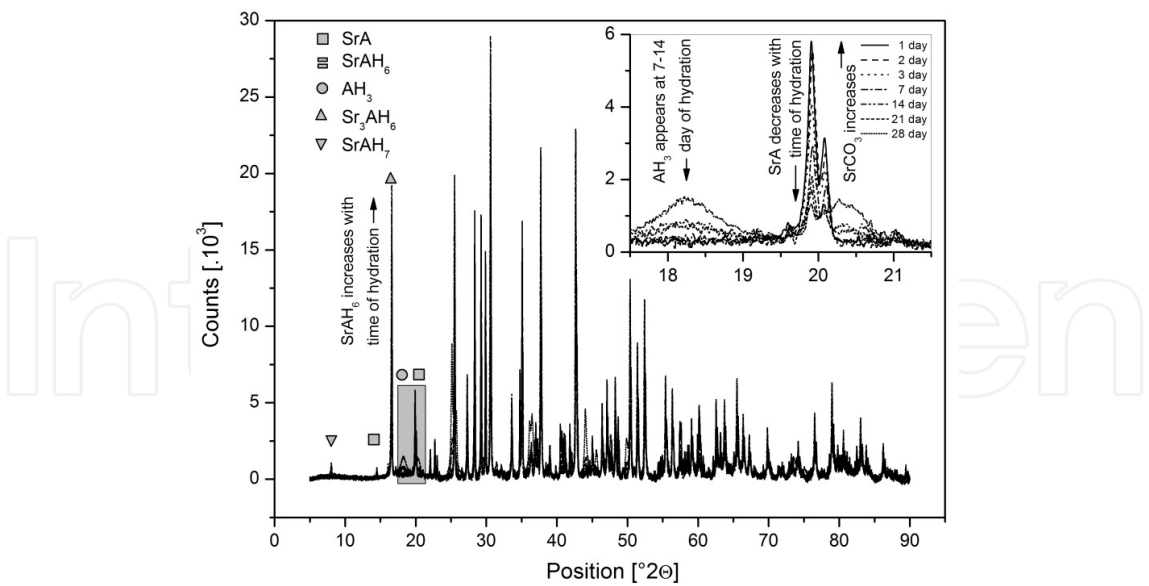


Figure 1. Hydration of strontium aluminate clinker upon the first 28th days hydration [379].

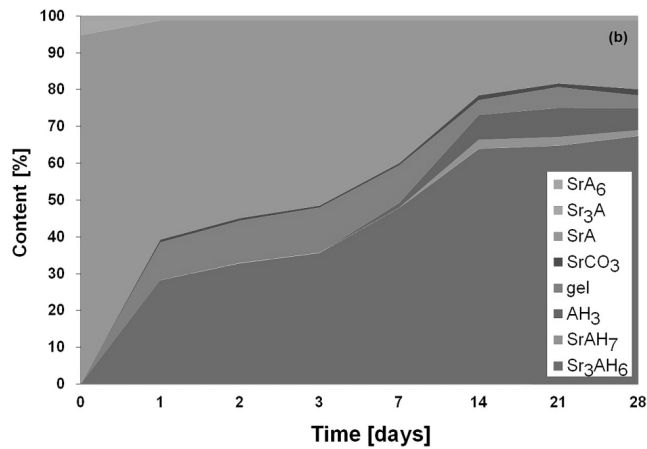


Figure 2. Course of hydration of strontium aluminate cement. The figure was constructed via the combination of XRD and TG-DTA results [379].

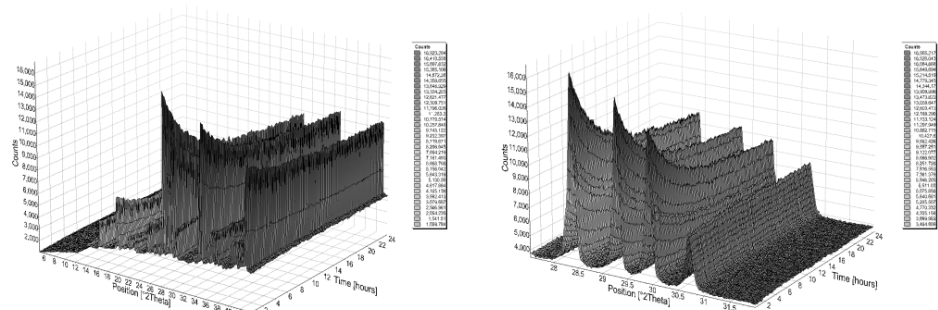


Figure 3. X-ray diffraction analysis upon early stage of hydration of strontium aluminate clinker.

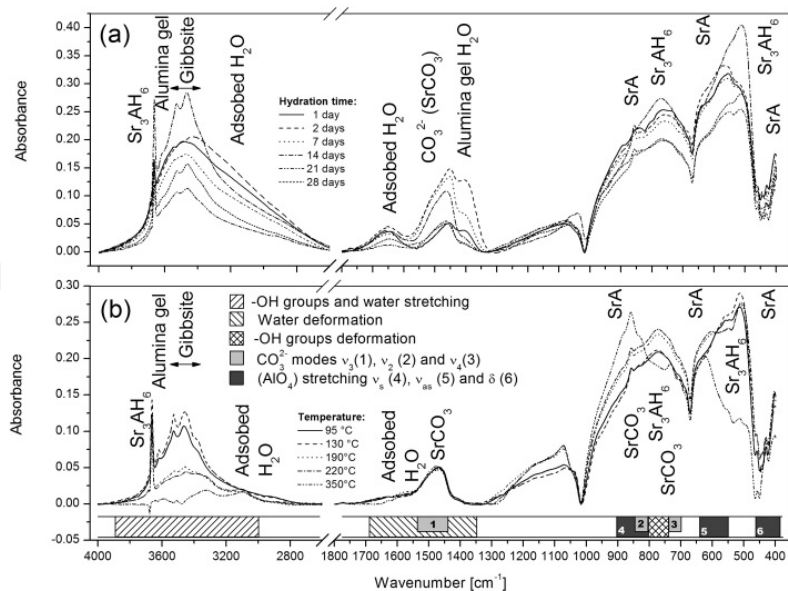


Figure 4. Infrared spectra of strontium aluminate clinker upon the first 28th days of hydration (a) and thermal treatment (b) [379].

The SEM pictures of strontium aluminate cement (a) and hydrated cement stone (b-d) during the first 28 days of hydration process are shown in Fig.6. Well-developed crystals of Sr₃AH₆ (b) precipitated and grew from super-saturated liquid phase of cement slurry before setting. The hydration products usually formed during the setting do not occur in well-developed rhombic dodecahedron of Sr₃AH₆.

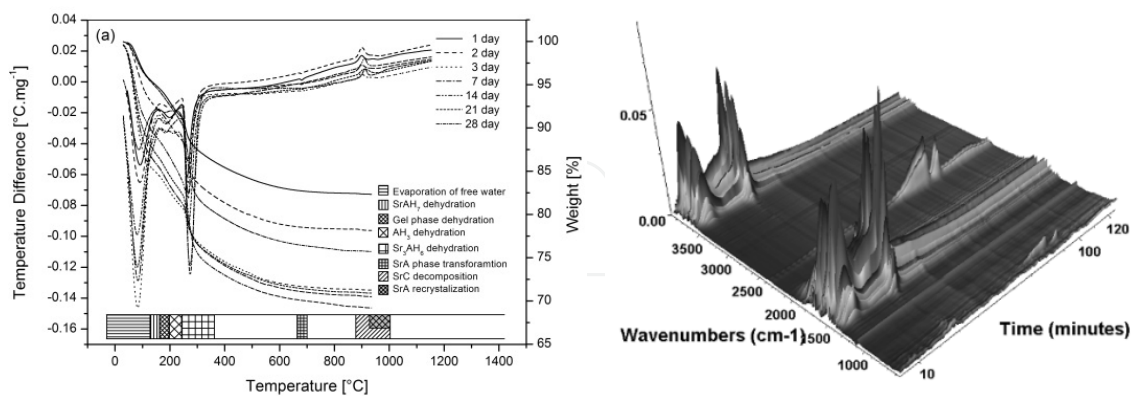


Figure 5. Thermal analysis of hydrated sample of strontium aluminate clinker performed at the heating rate of 10 °C min⁻¹ [379].

The SEM (Fig.6) picture of hydrated cement stone after 21 and 28 days of hydration shows well-developed Sr₃AH₆ crystals surrounded by kidney-shaped aggregates of SrAH₇ [379].

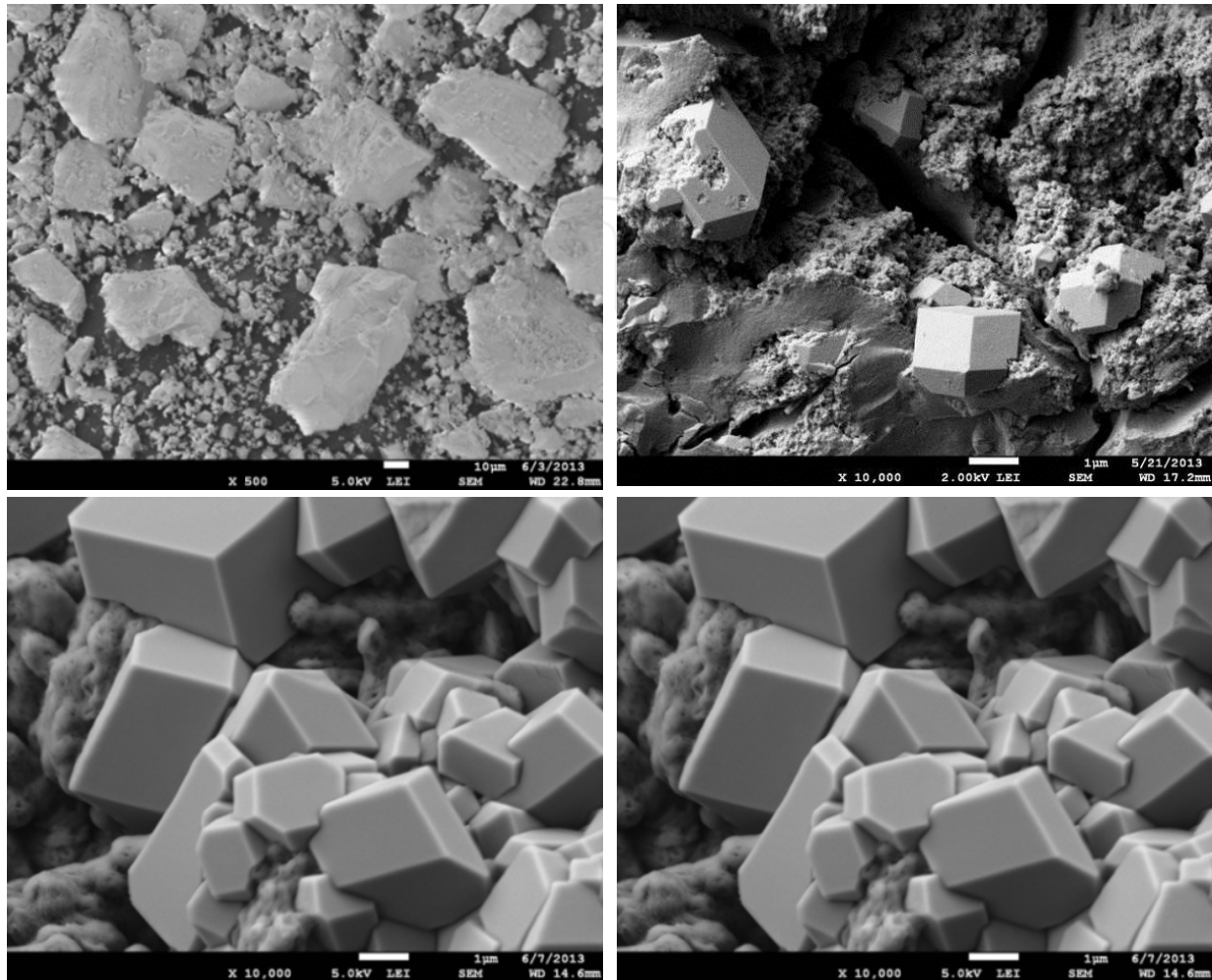


Figure 6. SEM pictures of strontium aluminate clinker (a) and hydrated cement stone after 3 (b) and 21(c) and 28(d) days of hydration process [379].

2. Hydration and activation energy of hydration

Fig.7 shows the heat flow in the combination with the heat of hydration of strontium aluminate cement (a) and calcium aluminate cement (b, Secar 51) during 50 hours of hydration process at the temperature of 25 °C. Fast evolution of heat immediately after mixing with water is typical for strontium aluminate cement while 10 hours long induction period was measured for calcium aluminate cement. There isn't any induction period observed hence the hydration of strontium aluminate cement starts immediately after mixing of strontium aluminate cement with water and the heat flow then asymptotically decreases to the baseline. The main hydration reaction in calcium aluminate cement arises 13.5 hours after mixing with water.

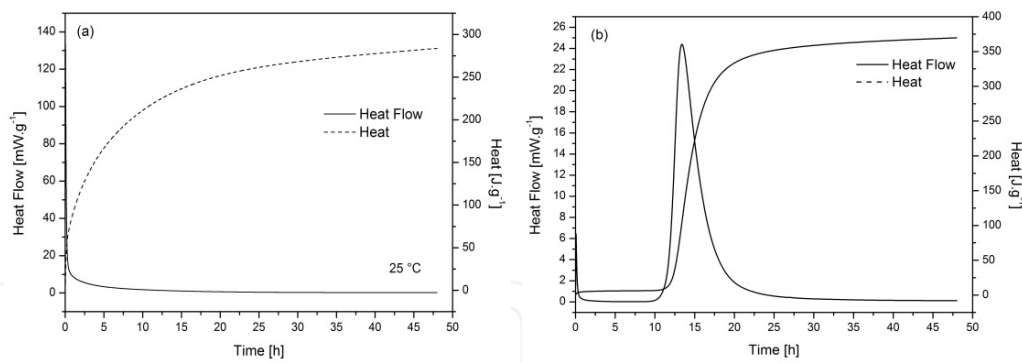


Figure 7. Heat flow and heat of hydration of strontium [379] (a) and calcium aluminate cement (b).

After the first 50 hours of hydration the heat flow of both cements already drops down to the baseline, but still produces 0.21 and 0.11 mW g⁻¹ for strontium aluminate and calcium aluminate cement, respectively.

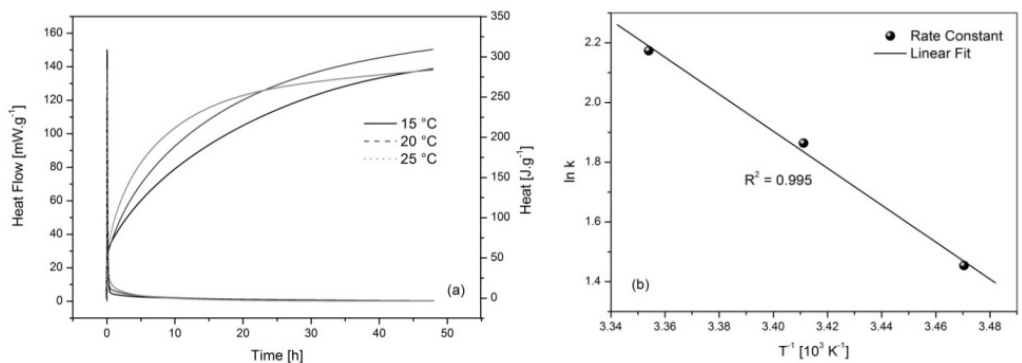


Figure 8. Arrhenius plot for the hydration of strontium aluminate cement.

The calorimetric assessments at the temperature of 15, 20 and 25 °C were applied in order to investigate the activation energy of hydration of strontium aluminate cement (Fig.8(a)). The apparent activation energy and the frequency factor of the process were calculated from the Arrhenius plot to be 51 kJ•mol⁻¹ and 2.55•10⁶ s⁻¹ (b), respectively. The D₄ kinetic equation was evaluated as the most probable mechanism of the process of hydration.

3. Setting behaviour and influence of temperature

The measurement of storage modulus, loss modulus and damping factor ($\tan \theta$) were performed in order to evaluate the behaviour of strontium aluminate slurry prepared with the water to cement ratio of 0.3 at different temperatures. The results (Fig.9) indicate that the setting time of strontium aluminate clinker is significantly reduced by increasing temperature.

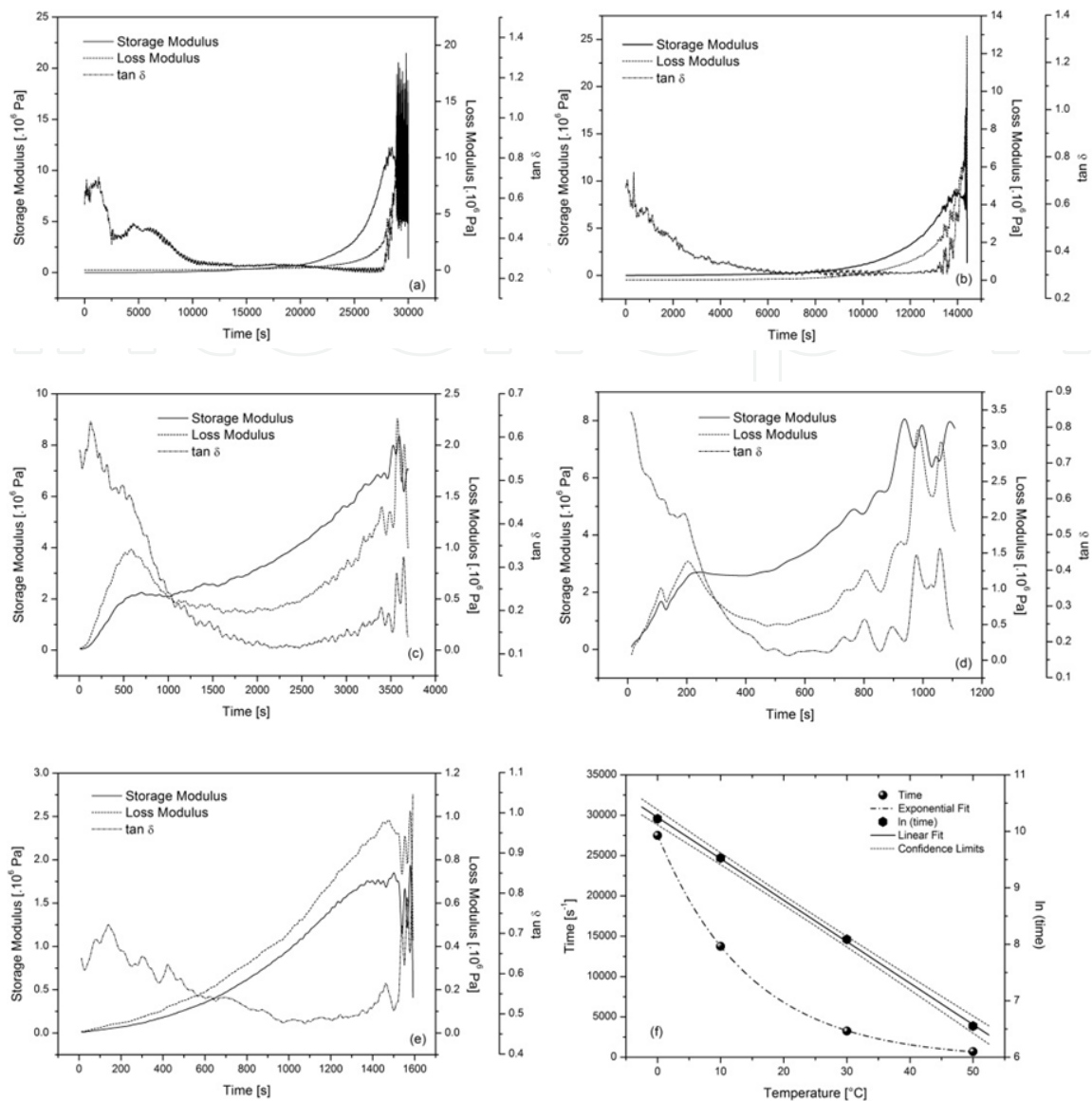


Figure 9. Tan delta for strontium aluminate clinker set at the temperature of 0 (a), 10 (b), 30 (c) and 50 °C (d) and influence of temperature on the setting time (f). The data for Secar 51 at 25 °C are shown in (e).

4. Improving mixture workability

Fast evolution of heat after mixing with water without the induction period is a disadvantage of strontium aluminate cement. In order to improve the cement workability the influence of some organic and inorganic compounds on the process of hydration was investigated by isothermal calorimetry. The formation of strontium chelates or buffer with organic acids, such as acetic and citric acid, or the formation of diffusion barrier on the surface of strontium aluminate grains via the introduction of sodium sulfate or boric acid are supposed.

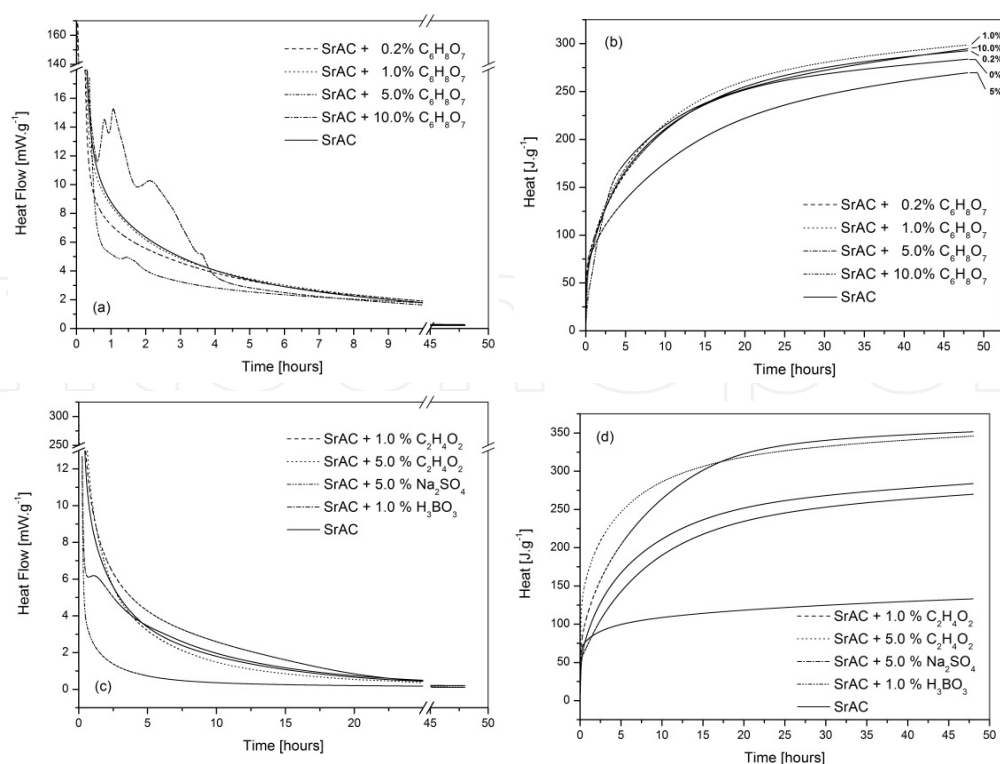


Figure 10. Calorimetry of strontium aluminate cement with acetic acid, citric acid, sodium sulfate and boric acid.

The effect of sulfates on the course of hydration of strontium aluminate cement is discussed in Chapter 8.2, but the addition of gypsum up to 5 % can improve the behaviour of cement during the hydration.

5. Chemical shrinkage

Chemical shrinkage¹ is defined as the absolute (internal) volume change of cement paste that results from the hydration of cementitious materials. Chemical shrinkage of strontium aluminate cement was evaluated using the pycnometric measuring technique described by Zhang et al. [674].

The shrinkage of cement slurry after mixing with water is shown in Fig.11. There are two linear parts, which can be extrapolated to the cross point at the time of 5.2 hours after mixing with water with corresponding volume shrinkage of 2.7 cm³/100g.

This change in the shrinkage direction should be explained as the turn of the hydration (chemical) shrinkage to the setting shrinkage² (7.3 cm³/100g). The cross point appearing at the time of 77.2 hours after mixing of SrAC with water is related to the formation of SrAH_x hydrate (where x=7-10, please consult with Fig.2) [379]. The total volume shrinkage of cement slurry reaches about 10 cm³/100g after 13 days of hydration.

¹ The deeper discussion on the chemical shrinkage can be found in Chapter 8.

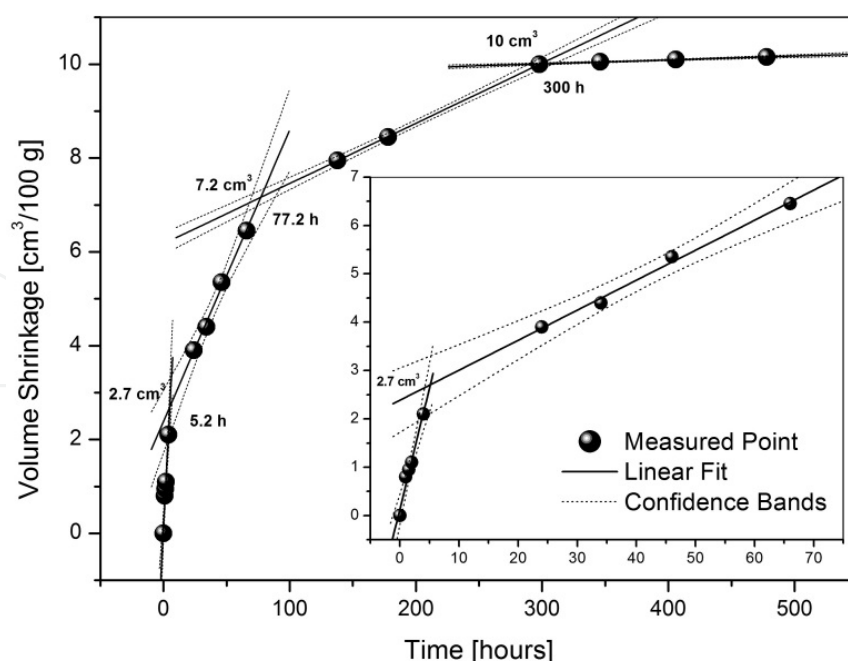


Figure 11. Early age volume shrinkage of strontium aluminate cement slurry.

6. Hydration of other phases in $\text{SrO-Al}_2\text{O}_3$ system

The tristrontium aluminate (Sr_3A) phase is more reactive than tricalcium aluminate (Ca_3A). There are two possible reasons for increased reactivity of tristrontium aluminate [8,416,417]:

1. Increased size of Sr^{2+} cations increases the size of channels within the Al_6O_8 rings allowing for more rapid diffusion of water.
2. Considerable overbonding at three Sr^{2+} sites occurs suggesting that there is considerable strain in $\text{Sr}_3\text{Al}_2\text{O}_6$.

The isothermal calorimetric experiments on the hydration of other strontium aluminate phases such as tri-strontium aluminate, strontium dialuminate and strontium hexaaluminate compared to strontium aluminate at the temperature of 25°C are shown in Fig.12. The calorimetric data show that cements based on tri-strontium aluminate phase have short induction periods. The main and second hydration effect arise at the time of 4 and 48 h after mixing with water. The main hydration effect drops down to the baseline at the time of 10 h and the second at the time of 60 hours.

2 Hydration is defined as a reaction of inorganic binder with water accompanied by setting and hardening. Setting is spontaneous conversion of cement slurry into solid body. Hardening is a process of gradual increasing of strength of cement stone after setting.

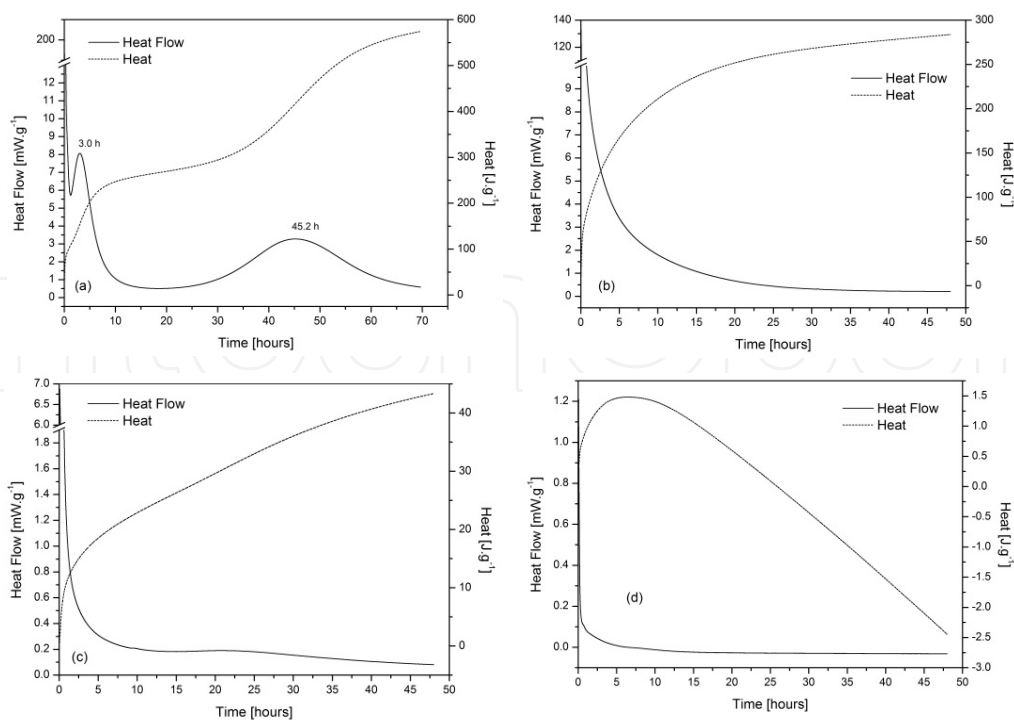


Figure 12. Heat flow and heat of hydration of tri-strontium aluminate (a), strontium aluminate (b), strontium dialuminate (c) and strontium hexaaluminate (d) at the temperature of 25 °C.

The heat of hydration decreases with decreasing strontium oxide/ aluminum oxide in the phase (Fig.13). According to the decrease of heat of hydration, the strontium aluminate phases should be ordered as follows:



It seems to be the sigmoidal dependence of heat on hydration, where the inflexion point corresponds to the strontium aluminate phase.

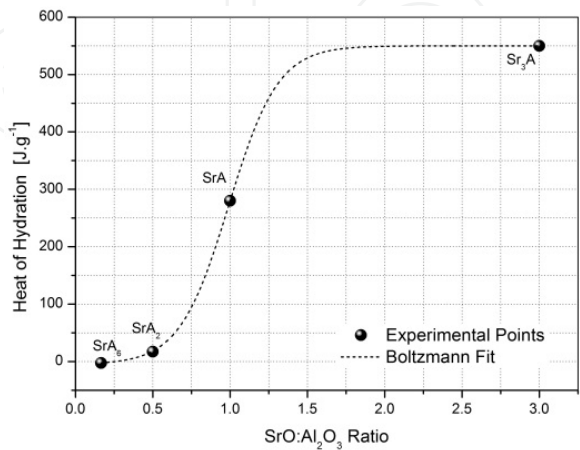


Figure 13. Hydration heat of strontium aluminate phases after the first 50 hours of hydration.

The heat flow of strontium aluminate phases is 0.58 (70 h), 0.21 (50 h) and 0.08 mW g⁻¹ (50 h) for tri-strontium aluminate, strontium aluminate and strontium dialuminate phase after the first 50 hours of hydration, respectively.

Tri-strontium aluminate hexahydrate is the only crystalline hydration product that can be recognized by X-ray diffraction analysis (Fig14).

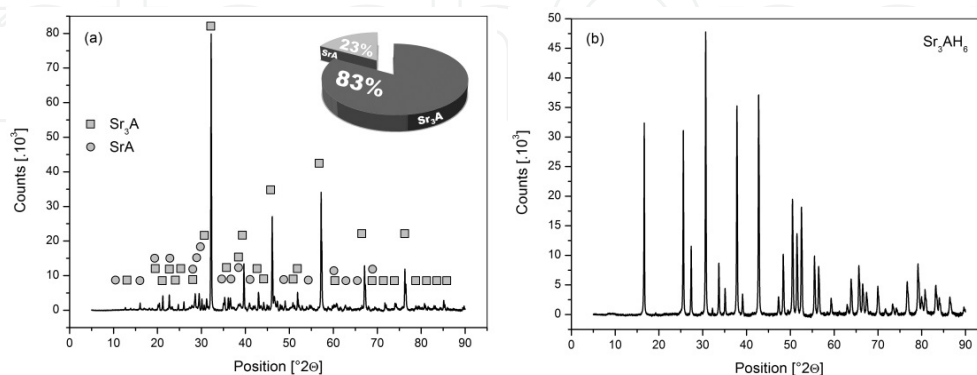


Figure 14. Ground clinker prepared from tri-strontium aluminate (a) and hydration products (b).

The results of thermal analysis of strontium aluminate clinker after the hydration are shown in Fig.15(a). The TG-DTA plot confirms that tri-strontium aluminate hexahydrate is the only hydration product of hydration of Sr_3A clinker. Please refer to Chapter 6.5 for the discussion of mechanism of thermal dehydration of tri-strontium aluminate hexahydrate.

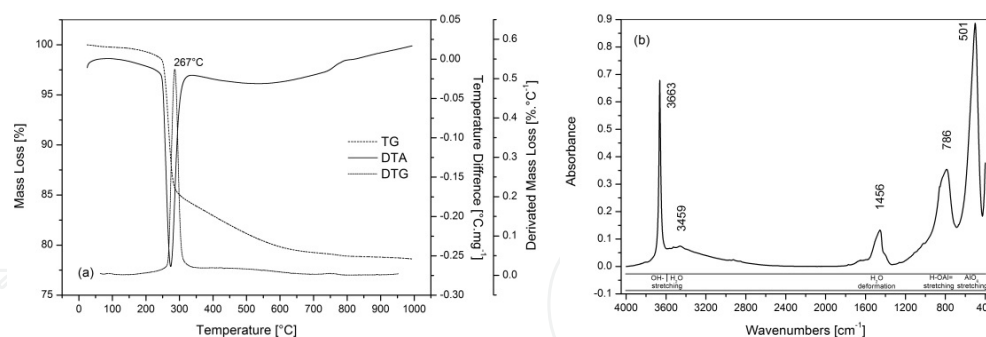


Figure 15. TG-DTA (a) and FT-IR (b) of hydrated cement stone.

The stretching of OH groups at 3663 cm⁻¹ in Sr_3AH_6 is the most characteristic feature in infrared spectrum of hydrated cement stone (Fig.15(b)). The deformation mode is located at the wavenumber of 1757 cm⁻¹. The bands located at 786 and 502 cm⁻¹ are most probably the composed bands of symmetric and antisymmetric stretching of =Al-OH groups [418,419,422] and the characteristic frequency of Al-O-Al stretching of AlO_6 octahedra [420,421,422], respectively.

SEM pictures of hydrated cement stone of ground tristrontium aluminate (Sr_3A) clinker are shown in Fig.16.

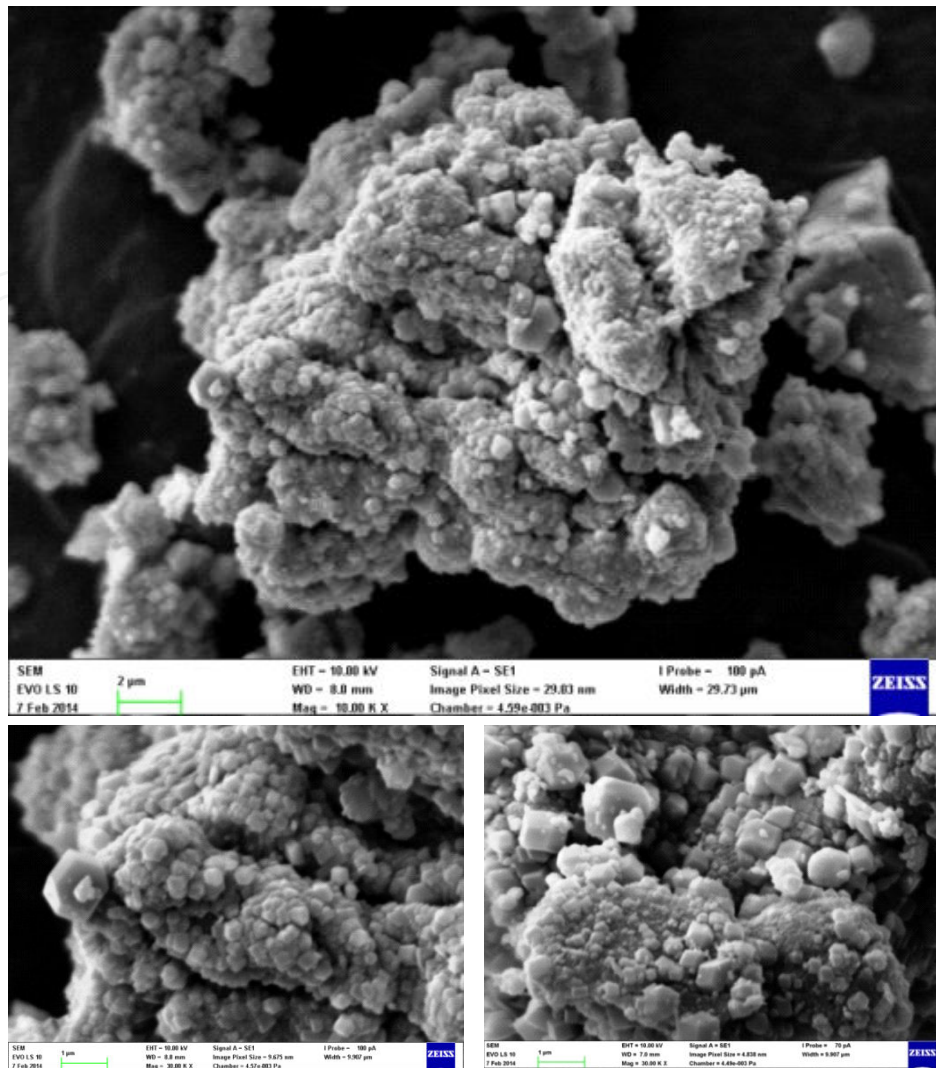


Figure 16. Tri-strontium aluminate hydrated cement stone after 72 h of hydration at 25 °C.

The hydrogarnet phase seems to be the only hydration product of Sr_3A (Fig.14), but the microphotographs show two main crystalline forms of the main product of hydration: icositetrahedron and hexagonal plates. Icositetrahedron are early forms precipitated from supersaturated solution, while hexagonal shapes are formed during later stage of hydration process.

Therefore the hydration process of tristrontium aluminate clinker should be described by the following chemical equation:



which corresponds to the theoretic w/c ratio of about 0.21. This value is lower than theoretic water to cement ratio (Eq.1) calculated for strontium aluminate clinker (0.36).